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Review

## Voltammetry in solutions of low ionic strength. Electrochemical and analytical aspects

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### Abstract

Recent progress in microelectrode voltammetry in solutions without or with low concentrations of supporting electrolyte is reviewed. The following points are addressed: mathematical treatment of transport, experimental setup, steady state and non steady state transport, migration coupled with homogeneous equilibrium, voltammetry in undiluted redox liquids, studies on the mechanism of the electrode processes, transport of ions in solutions of polyelectrolytes and colloids, and analytical applications. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Voltammetry; Migration; Microelectrodes; Low support ratio; Absence of supporting electrolyte

### 1. Introduction

Voltammetric measurements in solutions of very low ionic strength, including those without deliberately added supporting electrolyte, became possible by using microelectrodes, electrodes with at least one essential dimension in the range of micrometers or less. Voltammetric measurements without supporting electrolyte departed significantly from the traditional way such measurements were performed. 'Traditional' voltammetry required an excess of electroinactive ions to make the solution sufficiently conductive, to make a compact double layer, and to suppress migration of electroactive species. Electrode processes at microelectrodes are usually associated with very low currents in the range of nano- or picoamperes. Consequently, it might seem straightforward that even in solutions of very high resistance, the ohmic *IR* drop is very low. However, there is one specific phenomenon which contributes to

lowering of the ohmic drop. This is an increase in ionic strength in the depletion layer while the electrode reaction of an uncharged substrate advances. The ionic strength increases as a result of the formation of the charged products accompanied by drawing of appropriate amounts of counterions from the bulk solution. This allows voltammetric measurements in solutions of low conductivity, e.g. solutions without added supporting electrolyte or simply solutions of low support ratio,  $\gamma$ , which is the ratio of the concentration of supporting electrolyte to the concentration of the reactant. It should be mentioned here that it is possible to have both a relatively high conductivity and a low support ratio; this is the case with a very high concentration of electroactive species. For neutral reactants, the use of regular-size electrodes, with sizes in the range of mm, was practically not possible in solutions of low ionic strength. Consequently, some media that were not accessible for voltammetric studies are now open for measurements with microelectrodes. Eventually, the experimental interest in no supporting electrolyte voltammetry triggered work on development of rigorous mathematical models.

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Measurements without supporting electrolyte were initiated already in the 1930s, in parallel to the growth of polarography [1,2]. However, those basic studies were limited to ionic species. Instrumentation was poor, and insufficient attention was given to the presence of adventitious, unwanted ions in the solutions.

There is a number of reviews on the characterization and application of voltammetry with microelectrodes [3–14]. The recent intensive progress in the area of voltammetry in low ionic strength media inspired us to present an overview of the current status and opportunities for electroanalytical techniques in media of low support ratio. The following aspects are selected and discussed in this paper: mathematical treatment of transport, experimental setup, steady-state, non steady-state and convective voltammetry, migration coupled with homogenous equilibrium, voltammetry in undiluted liquid organic substances, studies on the mechanism of the electrode processes, studies in polyelectrolytes and colloids, and analytical applications.

## 2. Mathematical treatment of transport

Under steady state conditions, a spherical diffusion field is formed at the surface of disk- or spherical (hemispherical) microelectrodes. This and substantial mathematical simplifications are accountable for choosing of the transport equations in spherical coordinates to model (in most theoretical treatments) migrational currents at microelectrodes. Consequently, before any comparison with the theory, experimental steady-state currents for disk microelectrodes should be corrected by a factor of  $\pi/2$ , while those obtained with hemispherical microelectrodes can be compared directly.

The transport of species  $i$  is described by its flux,  $J_i$ , according to the Nernst–Planck equation, which in the spherical coordinates can be written as:

$$J_i = -D_i \frac{\partial c_i}{\partial r} - D_i \frac{z_i F}{RT} c_i \frac{\partial \phi}{\partial r} \quad i = S, P, A \text{ or } C \quad (1)$$

where S denotes the substrate, P denotes the product, and A and C refer to the anion and the cation of supporting electrolyte, respectively.  $D_i$ ,  $c_i$  and  $z_i$  are the diffusion coefficient, concentration, and the charge of  $i$ th species, respectively.  $\phi$  is the electrostatic potential in the solution, and  $R$ ,  $T$ , and  $F$  have their usual meanings. Eq. (1) was used to model systems under steady- and non-steady state conditions [15–22]. As was shown by Oldham [17,18], it is convenient to transform Eq. (1) to the following form:

$$\frac{J_i}{2\pi D_i} = \frac{\partial c_i}{\partial \left(\frac{1}{r}\right)} + \frac{z_i F}{RT} c_i \frac{\partial \phi}{\partial \left(\frac{1}{r}\right)} \quad (1a)$$

to obtain the total flux across the hemisphere of radius  $r$ . This flux is not only invariant with time, but is also uniform in space.

The transport dynamics of each species is described by the following equation:

$$\frac{\partial c_i}{\partial t} - D_i \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} \right) - D_i \frac{z_i F}{RT} \left( c_i \frac{\partial^2 \phi}{\partial r^2} + \frac{\partial c_i}{\partial r} \frac{\partial \phi}{\partial r} + \frac{2c_i}{r} \frac{\partial \phi}{\partial r} \right) = 0 \quad i = S, P, A \text{ or } C \quad (2)$$

and this equation together with appropriate boundary conditions is used to calculate the transient currents, see for example Refs. [23–26].

The first successful attempt to predict the current for the reduction of a cation (or the oxidation of an anion) in the absence of supporting electrolyte was presented by Amatore et al. [15]. The authors used Eq. (2) in an equivalent form for cylindrical diffusion, and by employing the Nernst layer approach and assuming the steady- or quasi steady-state conditions they obtained a solution, which was correct for all types of microelectrodes. This was shown in their next paper [16], in which the mathematical solution was extended to all simple electrode processes. The same year, using Eq. (1a), Oldham presented a more rigorous treatment, including the analysis of the ohmic drop [17]. After assuming that the electroneutrality principle is obeyed, it can be shown that the total solute concentration ( $\Sigma c_i$ ) is uniform throughout the solution [15,17,18].

Steady-state theoretical voltammograms can be also obtained by using the chronopotentiometric approach and assembling the  $I$ – $E$  pairs [27].

If the electroneutrality principle is not obeyed (see the discussion in Section 2.1) then either Poisson's equation [28]

$$\frac{\partial}{\partial r} \left( \frac{\partial \phi}{\partial r} \right) = -\frac{F}{\varepsilon \varepsilon_0} \sum_j z_j c_j(r, t) \quad (3)$$

or the equivalent displacement current equation [29] must be used to treat the electrical migration problems. Generally, to solve any system of equations that contains Eq. (2) and possibly Eq. (3) one should turn to digital simulation. Successful implementation of various digital simulation methods can be found for example in Refs. [24,28,29]. (See also the references in Sections 5.1, 5.2 and 7.)

### 2.1. Electroneutrality

It is usually assumed that the electroneutrality principle is obeyed at any point in the solution ( $\Sigma c_i z_i = 0$ ). Norton et al. [28] have shown that this principle does not hold when the depletion layer is entirely or in a significant part included in the double layer. On the

basis of their data, one can make the following conclusions. The depletion layer thickness can be estimated as  $10r_0$ , where  $r_0$  is the electrode radius, and the thickness of the double layer is ca.  $5\kappa^{-1}$ , where  $\kappa^{-1}$  is the Debye–Hückel length,  $\kappa^{-1} = (ee_0kT/2c^0z^2e_0^2)^{1/2}$ , where  $c^0$  is the bulk  $z:z$  electrolyte concentration. For a univalent electrolyte in aqueous solution, the approximate  $\kappa^{-1}$  values are 10 nm, 100 nm and 1  $\mu\text{m}$  for concentrations of  $10^{-3}$ ,  $10^{-5}$  and  $10^{-7}$  M, respectively. This thickness will diminish significantly if the electrode potential departs from the potential of zero charge by more than 0.02 V. For the usual sizes of microelectrodes ( $r_0$  larger than 1  $\mu\text{m}$ ), and the concentration of electrolyte not lower than  $10^{-6}$  M, the double layer thickness becomes insignificant compared to the depletion layer thickness (note that an ion concentration of  $10^{-6}$  M is very often that of a solution without deliberately added supporting electrolyte). On the other hand, if the radius of the electrode is smaller than  $\sim 0.1$   $\mu\text{m}$ , violation of the electroneutrality principle may occur in the presence of excess supporting electrolyte [30].

There is a kind of contradiction between the electroneutrality principle assumed in calculations and the existence of a potential gradient. The latter may be interpreted in terms of a separation of charges. However, the magnitude of this separation is very small, and therefore, it does not influence the concentration profiles significantly. For example, the typical excess of the charge, measured as  $\Sigma c_i z_i$  can be estimated as lower than 0.1% of the substrate concentration.

## 2.2. Resistance and the potential gradient

The value of the electrostatic potential,  $\phi$ , is macroscopically observed as an ohmic drop associated with the current flow through the solution. The magnitude of the ohmic drop can be calculated as the product of current ( $I$ ) and resistance ( $R$ ). The first successful attempts to estimate  $\partial\phi/\partial r$  for the modeling of voltammograms were shown by Amatore et al. [15,16] and Oldham [17]. Amatore et al. [15] transformed the Nernst–Planck equation to show the properties of the electric potential gradient. Both Amatore et al. and Oldham have noted that under steady state conditions and for equal diffusion coefficients it is possible to eliminate the electric potential gradient by summing the fluxes for individual ions (Eqs. (1) and (1a)) and using the electroneutrality principle. The resistance of the cell without excess supporting electrolyte changes while the electrode process advances, therefore the static resistance, which can be expressed as:

$$R_{\text{static}} = \frac{RT}{2\pi F^2 r_0 \sum_i c_i^0 z_i^2 D_i} \quad (4)$$

cannot be used for estimation of the ohmic drop. Eq. (4a) presents how, for example, the cell steady state resistance,  $R_{\text{ss}}$ , changes with current,  $I$ , for the oxidation of an uncharged substrate, S, under the conditions of deficiency of supporting electrolyte [17].

$$R_{\text{ss}} = \frac{RT}{IF} \ln \left[ 1 + \frac{D_S c_S^b I}{2D_P c_C^b I_l} \right] \quad (4a)$$

where  $I_l$  is a limiting current,  $P$  is product of the electrode reaction and  $C$  is a counterion. The ohmic drop during electrolysis with an excess supporting electrolyte is a function only of the flowing current.

Before steady-state is reached, for a low concentration of electrolyte, both current and resistance change with time. The resistance depends on ion distribution in the cell, which changes with time. This can be effectively examined using digital simulation. To simulate the ohmic drop at any point in the solution, it is necessary to know the local resistance of a region located between two appropriate closest hemispheres [23–25]. The resistivity of such a region is assumed to be constant during a time interval,  $\delta t$ , and the resistance can be written as:

$$R_j = \frac{\rho_j \frac{dr}{2\pi r^2}}{\frac{RT}{2\pi F^2 \sum_i z_i^2 D_i c_i(r_j)}} \cong \rho_j \frac{\frac{dr}{2\pi r^2}}{\frac{RT}{2\pi F^2 \sum_i z_i^2 D_i c_i(r_j)}} = \frac{\rho_j}{2\pi} \left( \frac{1}{r_{j-1}} - \frac{1}{r_j} \right) \quad (5)$$

for  $j = 1, \dots, n+1$

and

$$R_j = \frac{RT}{2\pi F^2 \sum_i z_i^2 D_i c_i(r_0)} \left( \frac{1}{r_0} - \frac{1}{r_{\text{mid}}} \right) \text{ for } j = 0 \quad (6)$$

where  $r_1 \leq r_j \leq r_{\text{max}}$ ,  $r_0 < r_{\text{mid}} < r_1$ . The  $r_0$ -value corresponds to  $j = 0$ , and  $r_{\text{max}}$  to  $j = n+1$ . The parameter  $r_{\text{mid}}$  is chosen arbitrarily as  $r_0 + \delta r/2$ .

The potential drop at any point of the considered space can be obtained by multiplying the value of the flowing current (which equals the current passing through the electrode surface) by the resistance measured from the infinity to the point of consideration. This resistance can be calculated by means of the formula

$$\begin{cases} R_{n+1}^{\text{tot}} = R^0 \\ R_j^{\text{tot}} = R_{j+1}^{\text{tot}} + R_j \end{cases} \quad j = n, \dots, 0 \quad (7)$$

where

$$R^0 = \int_{r_{\text{max}}}^{r \rightarrow \infty} \rho \frac{dr}{2\pi r^2} = \frac{RT}{2\pi F^2 r_{\text{max}} \sum_i c_i^0 z_i^2 D_i}$$

is the resistance of the bulk solution, and  $R_j$  is given by Eqs. (5) and (6). The usual assumption that the distance

between electrodes is infinite determines the upper limit of the above integration ( $r \rightarrow \infty$ ). Practically, this assumption is valid (with an error of ca. 0.6%) when the second electrode is placed within a distance ten times larger than the depletion layer thickness,  $r_{\max}$ . The formula for the cell resistance in the form of Eq. (7) makes this variable independent of the chosen size of the simulation space,  $r_{\max}$ .

### 3. Experimental

To obtain reliable and reproducible voltammetric data in solutions of low conductivity, certain requirements must be met. The concentration of electroinactive ions in the solution should be well controlled, since both the wave height of an ionic reactant and the transient currents of uncharged reactants depend on this concentration. Maintaining the concentration of ions constant is especially difficult when the support ratio is very small. Usually the reference electrode is the main source of unwanted ions. To eliminate a possible leakage from the reference electrode several approaches can be applied. One possibility is to use an electrolytic bridge filled with deionized water or appropriate solvent; this method requires a high-input-impedance potentiostat. The second way is to use a quasi-reference electrode such as a Pt electrode; the drawback here is a 20–30 mV uncertainty in the potential measurement. However, wave heights are well reproducible [31]. Another way is to use an internal reference, e.g. ferrocene or a similar compound [19]. Traces of polishing materials such as aluminum oxide remaining at the microelectrode surface may lead to an increased level of ions in some media; therefore, it is advisable to use diamond water-based suspensions.

Experimentally obtained half-wave potentials in solutions without electrolyte usually depart from the real electrode potentials by the quantity  $IR$ . In practice, the magnitude of  $IR$  depends not only on the support ratio, but also on the type of the solvent (by means of its dielectric constant [32]) and on the reactant.

Potentiostats used for voltammetric experiments in solutions of low ionic strength should be characterized by a very high input impedance without compromising on the speed. Unfortunately, most of the inexpensive instruments available on the market do not handle measurements well in very resistive media, especially when the electrolytic bridge is filled with deionized water or a pure solvent.

### 4. Steady-state voltammetry

A very useful feature of voltammetry at microelectrodes under steady-state conditions and with excess

supporting electrolyte is a very simple expression describing the steady-state current:  $I_{\text{SS}} = knFDcr_0$ , where  $r_0$  is the electrode radius,  $D$  is the diffusion coefficient,  $c$  is the concentration of the electroactive species, and  $k$  is a parameter which equals 4 for disk electrodes and  $2\pi$  for hemispherical electrodes. Voltammetric curves for electroactive ions in solutions without supporting electrolyte are affected by a substantial contribution of migration, and therefore, the parameter  $k$  may change significantly. However, the steady-state currents of uncharged species are unaffected by migration. Since the migrational contribution to the current depends on such factors as the number of electrons transferred, the charge of the reactant and the support ratio, the number of possible situations, or in other words, the number of  $k$ -values is almost unlimited. An overview of theoretical problems related to the modeling of voltammograms without supporting electrolyte has been presented in the previous section of this paper; here we would like to focus on the results of theoretical and experimental investigations. From an instrumental point of view, as was discussed in Section 3, the most demanding are the cases of uncharged reactants. The first experimental papers on voltammetry of uncharged species without added supporting electrolyte were published in 1984 [33,34], and analytical aspects of such voltammetry were presented in Ref. [35].

The theory for simple electrode processes for electroactive ions under steady-state conditions seems to be well developed. Both theoretical treatments and experimental data for the ratio of the limiting to the diffusional current without and with any concentration of supporting electrolyte for different types of reactions and various charges of counterions are available in the literature. Special credit here should be given to Amatore et al. [16] who published the first paper on this subject and presented universal expressions for currents flowing at microelectrodes. Four final equations provided by Amatore et al. covered all the cases of charge increase, decrease and charge reversal. Oldham's theoretical paper on the subject appeared in the same year (1988), however, it was limited to only two cases [17].

Based on these theoretical predictions, if a  $+1$  cation from the salt with a  $-1$  anion (counterion) is reduced in solution without and with excess of univalent supporting electrolyte, the corresponding ratio of the voltammetric wave heights is 2. The presence of a  $-2$  counterion diminishes the wave height without supporting electrolyte by 25%, and the corresponding wave height ratio drops to 1.5. The most complete tables of the ratio of the wave heights and shifts in the half-wave potentials are given in Ref. [18]. The above theoretical relations change if diffusion coefficients of the reactant and product differ significantly [27]. For example, for the case of the charge decrease the theory predicts a moderate (within several percent) increase of the current when the support ratio decreases. However, when the diffusion coefficient of the

product is very high, the increase of the current is much larger than that predicted for equal or comparable diffusion coefficients, see Fig. 1. This phenomenon is caused by the fact that the fast diffusional removal of the product is compensated (partially) by the higher transport rate of the reactant. When the diffusion coefficient of the product is lower than that of the reactant, the product is accumulated near the electrode surface, impeding the transport of the reactant. When the diffusion coefficient ratio becomes very small, the product accumulation can suppress the limiting current almost entirely.

A general analytical expression, developed using Oldham's model [18], for a charge neutralization reaction, describing the ratio of the total limiting current,  $I_l$ , to the diffusion-limited current,  $I_d$ , for the reduction of  $M^{m+}$  to form P, in a solution of salts  $M_z Y_m$  and  $C_a A_k$  (used as supporting electrolyte), which includes the ions  $Y^{z-}$ ,

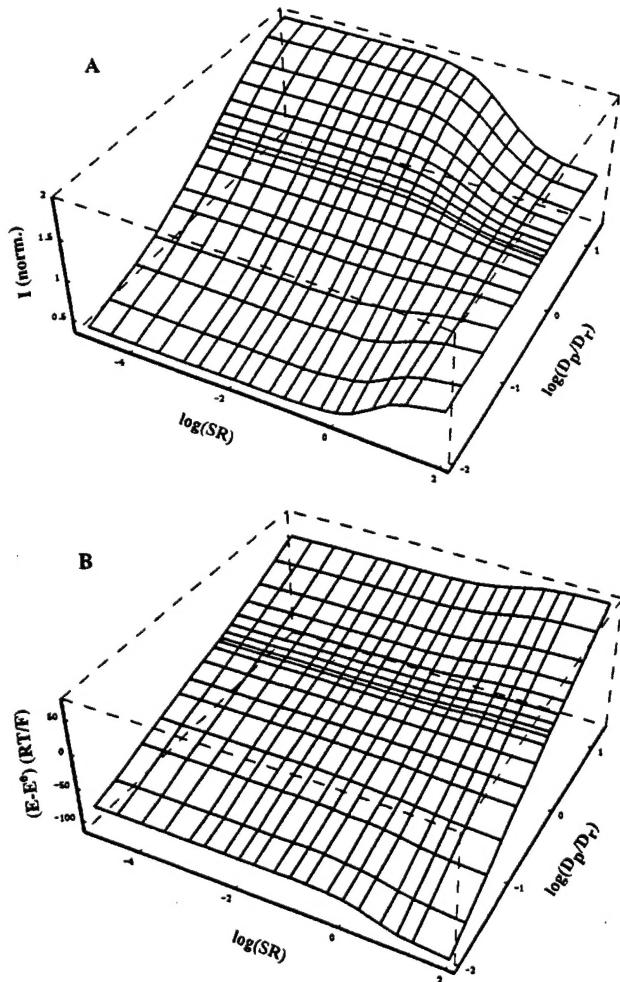


Fig. 1. Dependence of the limiting current (1A) and the half-wave potential, in mV, (1B), of steady-state  $I-E$  curve on the logarithm of the ratio of supporting electrolyte/reactant concentration,  $\log SR$ , and on the ratio of diffusion coefficients of the product and the reactant for the case of charge decrease. Diffusion coefficients of supporting electrolyte ions are assumed to be equal to the diffusion coefficient of the reacting ion. (Reprinted with permission from Ref. [23]. Copyright 1995 Elsevier Science.)

$C^{k+}$  and  $A^{a-}$ , is [36]:

$$-I_l/I_d = [(z+m)/z](x^z - 1) - [(k-m)/m]\gamma(x^{-k} - 1) + [(a+m)/am]k\gamma(x^a - 1) \quad (8)$$

where  $x$  is given as the solution to:

$$x^{(z+1)} - k\gamma x^{(1-k)}/m + k\gamma x^{(a+1)}/m = 0 \quad (9)$$

and  $\gamma$  is the ratio of bulk concentrations of the cation of supporting electrolyte,  $C^{k+}$ , and the electroactive ion,  $M^{m+}$ .

For a sign reversal reaction (substrate positive and product negative, and vice versa) such an expression does not exist, since the wave plateau does not develop [16,18] (in other words the ratio  $I_l/I_d \rightarrow \infty$ ), and for a sign retention reaction (both substrate and product positive or negative) the expression for the ratio of the wave heights without and with supporting electrolyte has the form [18]:

$$\frac{I_l}{I_d} = \frac{z_C - z_R}{z_C} \left[ 1 + \frac{z_R z_P}{z_C(z_R - z_P)} \ln \left\{ \frac{z_R(z_C - z_P)}{z_P(z_C - z_R)} \right\} \right] \quad (10)$$

where  $z_C$ ,  $z_R$  and  $z_P$  are the charges of the counterion, reactant and product, respectively.

The theoretical predictions were examined experimentally using several metal complexes by Cooper et al. [20]. These compounds gave an opportunity of studying various charged substrates, and a wide range of electrode reactions including various numbers of transferred electrons. Reduction of anions and both oxidation and reduction of cations were investigated. In most cases, the agreement with theoretical predictions was remarkably good. In several cases, however, the waves which were well defined with excess supporting electrolyte, almost disappeared in its absence. The authors had no credible explanation for this phenomenon. The voltammetric waves presented generally satisfied the Tomes criterion of reversibility, confirming that the  $IR$  drop was small.

The voltammetric reduction of three metal cations: thallium, cadmium and lead, in solutions of various salts ( $TlNO_3$ ,  $Tl_2SO_4$ ,  $Cd(NO_3)_2$ ,  $Pb(NO_3)_2$  and  $CdSO_4$ ), containing either no supporting electrolyte or its various concentrations ( $LiClO_4$  and  $Ca(NO_3)_2$ ) has been investigated by Ciszkowska and Osteryoung [36] using mercury film microelectrodes. The influence of migration was studied over a wide range of concentrations of electroactive species and supporting electrolyte. As predicted originally [16,20] and presented in references [36],  $I_l/I_d$  values of 2 and 1.5 were obtained in solutions without and with excess supporting electrolyte for the reduction of  $Tl^+$  cation in the solutions with mono- and divalent anions, respectively. For the two-electron reduction of divalent cations ( $Cd^{2+}$  and  $Pb^{2+}$ ) these ratios were 3 and 2 in the presence of mono- and divalent anion, respectively. The agreement between the experimental

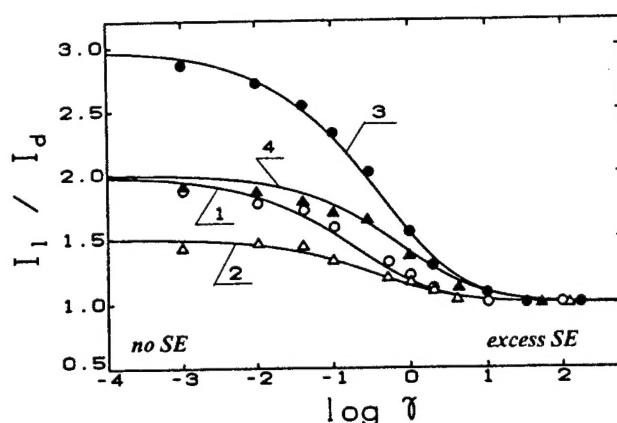


Fig. 2. Dependence of normalized wave heights,  $I_l/I_d$ , on the concentration of supporting electrolyte,  $\text{LiClO}_4$ .  $\gamma = c_{\text{SE}}/c_{\text{Me}^{+n}}$ , for 1 mM  $\text{TINO}_3$  (○), 1 mM  $\text{Tl}_2\text{SO}_4$  (△), 1 mM  $\text{Cd}(\text{NO}_3)_2$  (●), and 1 mM  $\text{CdSO}_4$  (▲). Solid lines – theoretical plots based on Eqs. (8) and (9) for  $\text{TINO}_3$  (1),  $\text{Tl}_2\text{SO}_4$  (2),  $\text{Cd}(\text{NO}_3)_2$  (3), and  $\text{CdSO}_4$  (4).

and theoretical data was very good, as shown in Fig. 2. Also, the simultaneous reduction of two electroactive cations in solutions without supporting electrolyte was studied. The 'exaltation' of the current was observed and the results were discussed in terms of theory of transport in solutions without supporting electrolyte. The 'exaltation' of the currents for the simultaneous reduction of a cation and a neutral molecule (e.g.  $\text{Na}^+$  and  $\text{O}_2$ ) was discovered in polarography independently by Kemula and Kolthoff [2]. Recently, this phenomenon has been modelled theoretically by Kharkats et al. [37].

The dependence of the current on the concentration of electrolyte for the reduction of metal cations has been reported also by Daniele et al. [38]. The authors have used solid (platinum and gold) and mercury microelectrodes to study the influence of a univalent supporting electrolyte on the voltammograms for such metal cations as  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in solutions with monocharged anions. A decrease in the concentration of supporting electrolyte resulted in an increase of the steady-state limiting current, poorly defined reduction waves, and broad and asymmetric stripping peaks. The ratio  $I_l/I_d$  without supporting electrolyte was 3 for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , and agrees well with the theoretical predictions and other experimental findings.

## 5. Migration coupled with homogeneous equilibrium

### 5.1. Reduction of strong and weak acids

The results of systematic experimental studies on the influence of supporting electrolyte on the steady-state reduction of hydrogen ion in solutions of strong and weak acids have been reported in a series of papers

[39–43]. For monoprotic strong acids in the absence of supporting electrolyte the reduction wave of hydrogen ion is twice the height of the wave in excess electrolyte solution [39,40]. Additionally, even in solutions of extremely low ionic strength (concentration of adventitious ions not higher than  $1 \times 10^{-6}$  M) the voltammetric wave is proportional to the concentration of acid. The dependence of the limiting current on the concentration of supporting electrolyte has been examined for many univalent supporting electrolytes. The experimental results have been found to agree very well with the existing theories. In solutions of polyprotic acids the influence of migration of  $\text{H}^+$  on the steady-state wave has been found to depend on the charge of the acid anion [42,43]. Consequently, for strong acids the ratio of the current without and with excess electrolyte has been found to be  $(1 + 1/n)$ , where  $n$  is the number of hydrogens in the strong acid molecule. Ratios very close to 1.5 and 1.25 have been observed experimentally for such strong polyprotic acids as  $\text{H}_2\text{SO}_4$  and  $\text{H}_4\text{W}_{12}\text{SiO}_{40}$ , respectively [42,43]. The same ratios have been obtained for polyprotic strong acids by Perdicakis et al. [44].

An interesting effect has been observed for the reduction of mono- and polyprotic weak acids in solutions without and with little supporting electrolyte [41,42]. Weak acids are only slightly dissociated, so their reduction currents should not be influenced by migration. It has been found, however, that the reduction wave of these acids depend strongly on the concentration of electrolyte, and the ratio of the limiting current without electrolyte to diffusional current is two, which was the ratio found previously for strong monoprotic acids. Additionally, it has been found that in solutions of low ionic strength the height of steady-state waves for reduction of weak monoprotic acids is proportional to the concentration of the acid over a wide range of concentrations; this can be used for analytical purposes. The height of the voltammetric wave diminishes with an increase of the concentration of supporting electrolyte, and the current drops much faster with addition of electrolyte than for strong acids.

Reduction of polyprotic weak acids in solutions without supporting electrolyte has been studied for two weak diprotic acids, oxalic and malonic, one triprotic acid, phosphoric acid, and one tetraprotic acid, pyrophosphoric acid [42]. It has been demonstrated that dissociated hydrogen ion and undissociated  $\text{HA}^{n-}$  anion can be reduced at Pt electrodes at the same potential (one steady-state wave) which is the case for oxalic and malonic acids, or in two voltammetric waves: phosphoric and pyrophosphoric acids. Strong dependences of  $I_l/I_d$  on the concentration and the kind of supporting electrolyte has been observed for all weak acids studied. The dependences found for oxalic and malonic acids are presented in Fig. 3. Theoretical interpretation of

this effect for weak acids is not trivial, and there is no comprehensive theory, although several models have been proposed [45–50]. The main differences between the theoretical treatments appear in the region of very low support ratios, which cannot be easily examined experimentally.

### 5.2. Complexation equilibrium

Voltammetric investigations of complexation equilibria in solutions with very low concentrations of supporting electrolytes eliminate the competitive complexation or contamination, make the activities of the species closer to their concentrations (which facilitates comparisons with the spectroscopic results), and finally, allow a broader range of concentrations of the species. Palys et al. [51] constructed theoretical voltammograms for ligands, metals and the complexes by employing either the extended theory of Myland and Oldham [22] or digital simulation. A wide range of complexes was examined, with the assumption that they are inert on the experimental time scale, which is often the case in host-guest chemistry and in macromolecular complexation. The calculated results show that the magnitude of the changes in the steady-state limiting current depends on the type of complexation equilibrium, the type of the change in the reactant charge number, and the complex formation constant,  $\beta$ . For the cases where migration contributes significantly to the transport, the relations between the measured steady-state limiting currents and  $\beta$  are given in the form of fitted equations. Those equations, in turn, can be employed for the determination of  $\beta$  from experimental results.

Experimental studies have been performed without added supporting electrolyte with an inert system con-

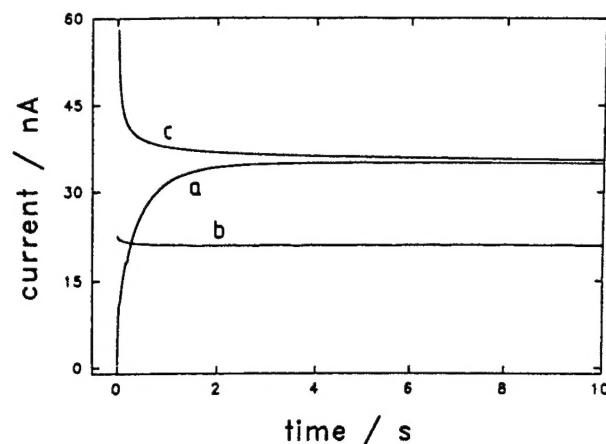


Fig. 4. Chronoamperometric curves in solutions saturated with oxygen; (a) pure water; (b) 0.1 M KCl and  $50 \text{ M}\Omega$  connected in series to the working electrode; (c) theory for excess supporting electrolyte. Pt microdisk,  $r = 11 \text{ }\mu\text{m}$ . (Reprinted with permission from Ref. [55]. Copyright 1995 Elsevier Science.)

sisting of europium (III) nitrate and 1,4,8,11-tetraazacyclotetradecane (cyclam) in a mixture of methanol and dimethylsulfoxide [52]. The complex stoichiometry (1:1) and the complex formation constant ( $\log \beta = 3.2$ ) have been determined in solution without electrolyte by nonlinear curve-fitting of the steady-state currents measured at a gold microelectrode for various concentrations of the ligand. Good agreement of those two values with the numbers obtained for excess supporting electrolyte supports the theoretical model presented in Ref. [51] and indicates that there are no additional interactions with the supporting electrolyte anion.

Daniele et al. [53] have demonstrated that the height of reduction waves of metal ions in solutions of low support ratio cannot be always predicted only from the charge of the free ion. Labile complexes may be formed with counterions accompanying the metal cation and with anions of added supporting electrolyte. Consequently, the influence of migration can be negligible, as presented for  $\text{HgCl}_2$ .

### 6. Non steady-state and forced convection

The traditional mode of voltammetric experiments with microelectrodes is steady-state voltammetry. However, the way the steady-state current is reached following an applied potential step, for example in chronoamperometry, is interesting and carries valuable information about the system studied. Transient ionic diffusion and migration to a disk electrode was modelled by Verbrugge and Baker [54]. However, particularly interesting is the reduction or oxidation of an uncharged substrate under the conditions of a low support ratio [23–26,55]. After applying an appropriate potential to the electrode, the current increases slowly,

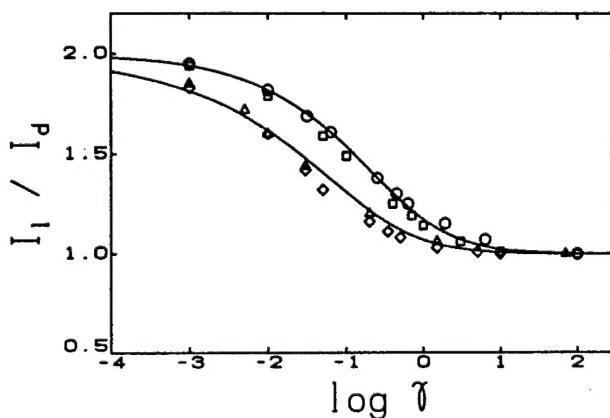


Fig. 3. Dependences of  $I_l/I_d$  for 1 mM oxalic ( $\circ$ ,  $\Delta$ ) and malonic ( $\square$ ,  $\diamond$ ) acids on the concentration of supporting electrolyte:  $\text{LiClO}_4$  ( $\circ$ ,  $\square$ ),  $\text{MgCl}_2$  ( $\Delta$ ),  $\text{Ca}(\text{NO}_3)_2$  ( $\diamond$ ).  $\gamma = c_{\text{SE}}/c_{\text{HA}}$ . Solid lines calculated according to Eqs. (8) and (9) for MY reactant and CA or  $\text{CA}_2$  supporting electrolyte. (Reprinted with permission from Ref. [42]. Copyright 1995 Elsevier Science).

and finally reaches the steady-state value, see Fig. 4. This increase is a result of the following phenomena: the counterions are accumulated at the electrode surface to neutralize the charge of the product formed, the resistance between the electrodes diminishes, and the electrode potential approaches the real value, which was set at the potentiostat. If there were no accumulation of ions and no corresponding changes in the resistance, the chronoamperogram would look like that obtained in 0.1 M KCl and with a 50 MΩ resistor connected in series to the working electrode, curve b. Curve c in Fig. 4 corresponds to the case of excess supporting electrolyte or, in other words, to purely diffusional transport.

The dependence of the current on time,  $I = f(t)$ , can be used to determine the electron transfer rate [24], various reaction stoichiometries in a variety of types of supporting electrolytes [26], and the total concentration of ions in the solution [25].

Gao and White [56] have investigated the influence of concentration of supporting-electrolyte on the steady-state voltammetric behavior of a rotating Pt disk microelectrode for several electrochemical reactions in acetonitrile. They demonstrated that the voltammetric response depends on the support ratio,  $c_{SE}/c_{red}$ , and on the charge of the reactant,  $z_{red}$ . For the oxidation or reduction of mono- and multicharged cations, voltammetric limiting currents increased linearly with the square root of an angular velocity,  $\omega^{1/2}$ , independently of the support ratio. For oxidation or reduction of neutral reactants, voltammetric currents were found to depend on both concentration of supporting electrolyte and an angular velocity. For  $c_{SE}/c_{red} \geq 0.1$  limited currents increased linearly with  $\omega^{1/2}$ , while for  $c_{SE}/c_{red} \leq 0.1$  those currents decreased with an increase in  $\omega$ . This behavior was interpreted by the authors in terms of the rate of migration of charge-balancing electrolyte ions to the electrode surface relative to the rate of removal of the same ions by forced convection.

Phenomena similar to those reported for rotating disks have been observed in a flow injection system combined with a low support ratio [57]. Increased convection at the electrode surface prevents sufficient accumulation of the counterions, and results in the decrease of the amperometric peaks with an increase in flow rate, which is opposite to the behavior seen in the presence of excess supporting electrolyte.

It has been found [58] that staircase voltammetric (SCV) peaks at regular electrodes for the reduction of metal cations without supporting electrolyte are less sensitive to the current-sampling parameter,  $\alpha$ , compared to those for purely diffusional transport. This is related to the increase of the uncompensated resistance with time. To obtain the SCV peaks of height identical to those of the linear scan peaks,  $\alpha$  should be set to 50% or the current should be measured at one half of the

pulse time. It has also been demonstrated that for an intermediate level of supporting electrolyte, the staircase waveform generates convectional transport to the surface of a hanging mercury drop electrode.

## 7. Voltammetry of undiluted liquid organic substances

The use of microelectrodes allows voltammetry of undiluted liquid substances such as pure solvents. This area of research has been introduced and developed mainly by White and coworkers [59–66]. It is interesting that despite a large concentration of undiluted reactant, ohmic potential drop in voltammetric experiments remains reasonably small. Voltammograms have been obtained for oxidation or reduction processes of several organic compounds, including nitrobenzene [59,60], 4-cyanopyridine [61], aniline and pyrrole [67], acetonitrile [68], simple alcohols [69], dimethylsulfoxide [70], and DMF [71]. Various interesting physicochemical aspects related to the voltammetry of undiluted liquids [62–64] have been reported and will be discussed in this paper. New analytical opportunities [69,70] have been found for the total electrolysis at the microelectrode surface, and for the voltammetric estimation of water levels in undiluted liquids. Interestingly, since the concentration of the reactant is so high, the influence of water and other impurities is practically eliminated. In the presence of either  $CCl_4$  or toluene, electroinactive species, a pre-wave appears for undiluted methanol, which might indicate that the methanol cation radicals interact strongly with those compounds [72].

It is impossible to perform voltammetry of undiluted substances without supporting electrolyte. A very low level of electrolyte, which results in a support ratio not higher than 0.001, helps to lower the ohmic potential drop and permits well defined voltammetric waves to be obtained.

The most specific feature of voltammetry of undiluted substances is the formation of a microlayer of an ionic liquid at the electrode surface. This microlayer is formed, because at the wave plateau the concentration of the substrate drops to zero, and the charged product is neutralized by the available counterion. At the electrode surface, the molar fraction of the substrate at the foot of the wave is 1; however, at the wave plateau while the molar fraction of the substrate is 0, the molar fraction of both the product and counterion is 0.5. This leads to a specific type of convection called diffusion-enhanced convection [61]. The formation of a very thin layer of ionic liquid leads also to strong changes in the viscosity of media and in activities and diffusion coefficients of all species near the electrode surface. Chemical changes, e.g. precipitation, are also possible. The ionic liquid layer formed by the electrooxidation of simple

alcohols with  $\text{LiClO}_4$ , and by the electroreduction of nitrobenzene, are apparently very stable, which results in stable steady-state current.

The investigation of the structure and properties of the depletion layer in such systems has been performed by White and co-workers [63,64]. The authors coupled electrochemical experiments with other techniques, such as interferometry [63] and elevated pressure [64]. It has been shown [63] that the changes in the optical distance can be used to determine the structure of the depletion layer; the effect of pressure on molecular transport rates has been demonstrated and it has been shown that the interfacial regions of the systems examined are compressible [64].

The first mathematical models describing the wave height of undiluted or very concentrated liquid substances were published by White and coworkers [61,65]. The wave height of undiluted substances at disk microelectrodes and in the appropriate time regime can be described similarly to the steady-state current for diluted reagents:  $I_{ss} = knFDcr_0$ . However, two problems should be mentioned. The first is the interpretation and estimation of the diffusion coefficient of the undiluted reagent. This diffusion coefficient diminishes significantly in the ionic microlayer at the electrode surface. The second one is related to the parameter  $k$ , which cannot be identical to that for diluted substrates. This is due to the diffusion engendered convection mentioned previously and changes in the viscosity at the electrode surface. A possible approach is to substitute the  $D$  value in the equation for  $I_{ss}$  with the bulk self-diffusion coefficient of the undiluted redox liquid. A rigorous digital model, based on this assumption and on the additional assumption of no specific interactions between the ions, has shown that the parameter  $k$  is a function of the ratio of volumes of the reagent and the counterion [73], and its value can be in the range from 1 to 4. For example, for anodic voltammetry of undiluted methanol with lithium perchlorate, the substrate and the counterion are of approximately equal volume, and therefore, the  $k$ -value is close to 2 and, as a consequence, the number of electrons transferred is 1. The influence of the size of counterions, added as tetraalkylammonium salts, TEAP, TPABF<sub>4</sub>, TBAP, and THAP, on the wave height of undiluted nitrobenzene is illustrated in Fig. 5. As predicted, the larger the cation (here the counterion, since the product is negatively charged) the higher is the limiting current. A different approach was presented by Ragsdale and White [66], who employed the Cullinan-Vignes equation to predict the reduction wave height of nitrobenzene in acetonitrile over the entire composition range. The deviations of experimental data from the theoretical predictions for  $x_{\text{NB}} < 0.4$  allowed detection of self-association of the solution components.

## 8. Studies on the mechanism of the electrode processes

The influence of the supporting electrolyte concentration on the kinetics and the mechanism of the electrode reactions has been studied for several systems. A very interesting review of the application of microelectrodes in kinetic studies, including some in solutions without supporting electrolyte and resistive media, has been presented by Montenegro [13]. Here we present some results on the influence of the support ratio on the kinetic of the electrode reactions. Beriet and Pletcher [74,75] investigated the dependence of the kinetics of such redox couples as  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$ , and  $\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}$  on the concentration of supporting electrolyte. They found that the shift in the formal potential with electrolyte concentration is significant, and demonstrated that the more highly charged the species the stronger the interaction with the counterion of the electrolyte. Without supporting electrolyte, the electron transfer reactions are slower. For the  $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}$  couples, the standard rate constants decrease by a factor of 2–5 (possibly due to a double-layer effect). These changes compared to the change for the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple, a decrease by a factor greater than 100, lead to the conclusion that there is a chemical decomposition of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  in solutions without excess cations, which results in the formation of an inhibiting film at the electrode surface.

Bento et al. [76] have studied the influence of the ionic strength on the current–potential response for the electrochemical reduction of a series of nitrobenzenes,

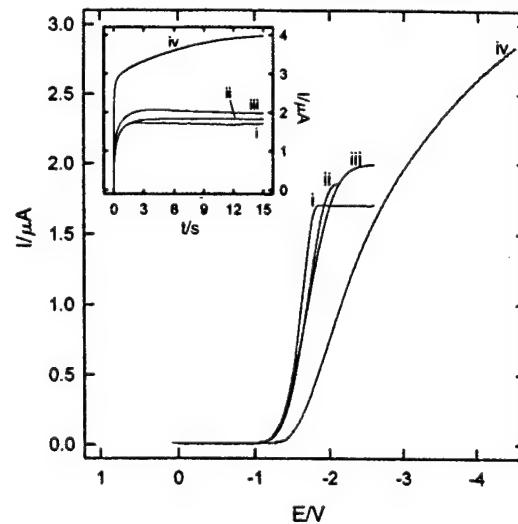


Fig. 5. Experimental voltammograms and chronoamperograms (inset) of undiluted nitrobenzene containing various supporting electrolytes: TEAP (i), TPABF<sub>4</sub> (ii), TBAP (iii) and THAP (iv); electrolyte concentration 0.01 M. Chronoamperograms recorded at potentials for the voltammetric wave plateau. (Reprinted with permission from Ref. [72]. Copyright 1998 American Chemical Society.)

nitrobenzene, nitrotoluene, bromonitrobenzenes, in aprotic solvents. Reproducible data have been obtained at microelectrodes in solutions of low ionic strength, including media without added supporting electrolyte. The results imply that the interactions between the anion radicals and the tetraalkylammonium cations are always weak; however, the cations interact strongly with more reduced intermediates.

Crayston and co-workers [77] have found that one-electron oxidation of arene- $M(CO)_3$  ( $M = Cr, Mo, W$ ) and thiophene- $M(CO)_3$  complexes in acetonitrile produces 17-electron cations  $(MeCN)_6M(CO)_6^{+ - n}$ , which undergo a rapid follow-up reaction. The intermediate  $(MeCN)_3Cr(CO)_3^+$  can be detected by voltammetry; however, reproducible voltammograms could be obtained only in solutions without supporting electrolyte. The authors found that the addition of electrolyte diminished the electrode response rapidly owing to electrode coating.

A numerical analysis of the sequential electron-transfer mechanism ( $A \rightarrow A^+ + e^-$ ,  $A^+ \rightarrow A^{2+} + e^-$ ) by Norton et al. [78] demonstrated that the rate at which  $A$  can be oxidized to  $A^{2+}$  depends on ionic strength of solutions. For low concentrations of supporting electrolyte this reaction is inhibited by the diffusional-migrational transport of generated  $A^+$  (produced within the depletion layer by the homogeneous bimolecular reaction) away from the electrode surface. This has been demonstrated for two experimental systems, the oxidation of tetrathiafulvalene (TTF) and the reduction of tetracyanoquinodimethane (TCNQ), over a wide range of electrolyte concentrations. In a subsequent effort, Norton and White [79] have examined two step reduction of methyl viologen ( $MV^{2+}$ ). They found that the magnitude of the second reduction wave increases with respect to the first with decrease of supporting electrolyte concentration, but with a slower rate than predicted by consideration of migration alone. This dependence of the current versus the support ratio was highly specific to the rate of the comproportionation of  $MV^{2+}$  and electrogenerated  $MV$ .

The theory for voltammetry of systems with the EE mechanism was proposed by Amatore et al. [80]. This theory was developed and tested with voltammetry of dicyano(fluoren-9-ylidene)methane and methylviologen dication. The agreement between theory and experiment was remarkably good. This paper was followed by a more general treatment of successive electron transfers in low ionic strength solutions [81]. This theory predicts that bimolecular electron transfer between members of the redox system that differ by +2 in oxidation state can influence strongly the magnitude of transport limited currents when ion migration contributes to molecular transport. Theoretical predictions were compared with experimental results for the two- and three-electron reduction of  $Ru(bpy)_3^{2+}$  in mixed acetonitrile + toluene

solutions; they agree very well.

Evidence for the adsorption of the cobaltocenium cation and precipitation of uncharged cobaltocene at the platinum microelectrode | acetonitrile interface without supporting electrolyte was reported by Cooper and Bond [82]. The anodic response at mercury microelectrodes can provide a fast and reliable diagnosis of adsorption or precipitation at the electrode surface in very diluted aqueous solutions without supporting electrolyte [83], as presented for the following compounds:  $NaBr$ ,  $NaCl$ ,  $Na_2C_2O_4$ ,  $NaOH$ , ethylenediaminetetraacetic acid,  $NaSCN$ ,  $NaNO_3$ , and thiourea.

Robertson and Pendley have studied the voltammetric behavior of quinone in dilute solutions of sulfuric acid with no added supporting electrolyte at platinum disk microelectrodes [84]. They have found that the process depends on the concentration of sulfuric acid relative to that of quinone. The one or two waves for the reduction of quinone were observed for higher and lower concentrations of acid, respectively. In another paper, Frank and Denuault [85] have used the reduction of hydrogen ion at a platinum microelectrode to study the relationship of both the proton concentration and the electronic charge versus the ionic strength during the oxidation of polyaniline films at a large electrode.

Microdisk electrodes have been applied to investigate the cathodic reduction of oxygen in purified water and in solutions with small amounts of neutral electrolytes [86,87]. All current–potential responses at Pt, Ag and Au microdisks gave well formed reduction waves for oxygen. It has been shown that several factors such as the lack of buffering capacity in the media, the high rate of mass transport to and from microelectrodes, the state of oxidation of the cathode surface and the uncompensated *IR* drop, influence the current responses. The work was initiated by the interest in developing a microdisk sensor for oxygen in media of low and perhaps, variable ionic strength.

Kadish and coworkers have examined solutions of  $C_{60}^{n-}$  ( $n = 0–4$ ) in aprotic solvents without supporting electrolyte [88]. Electrolyte was eliminated to avoid formation of ion pairs. Under these conditions the authors were able to detect the loss of at least two pyridine molecules from the solvation shell of the fullerene anions following each of the first two electroreductions.

Daniele et al. [89] have reported that using disk microelectrodes coated with Nafion® film permits investigation of mass transport within the polymer layer in solutions of low ionic strength, including those without electrolyte. Campbell et al. [90] have studied the potential window of tetrahydrofuran and propylene carbonate with a 10  $\mu m$  electrode without supporting electrolyte. The influence of such compounds as 2-methylfuran, 1,2-propanediol and water have been reported. The implications of the findings for the

secondary lithium cells have been discussed. Rolison and Stemple [91] have demonstrated the ability to drive catalytic processes when dc voltages are applied to low ionic strength dispersions for the selective partial oxidation of propene in an aqueous dispersion of Pd(II)–Cu(II) supported on Y zeolite.

The higher the concentration of supporting electrolyte, NaCl, the lower was the equilibrium constant for the disruption of the  $\alpha$ -ferrocenylundecyl- $\omega$ -hydroxy-polyoxyethylene micelles. This has been presented by Watanabe and co-workers [92] after examination of positive half-wave potentials of the micelles in aqueous solutions. The change in diffusion coefficients and aggregation numbers could not explain the large changes in the half-wave potential according to the equation derived by the authors.

It has been found that the measurement of rate constants of dissolution of AgCl can be performed in solutions without supporting electrolyte with greater precision compared to the situation where an inert electrolyte is present. Macpherson and Unwin [93] have used a probe ultramicroelectrode positioned close to a silver chloride surface (pressed pellet or electrochemically grown film) to induce and monitor the dissolution process via the reduction of  $\text{Ag}^+$ .

Barbero and Kötz [94] claim that electrochemical polymerization without supporting electrolyte would most probably result in a material with more reproducible and better defined properties, and is therefore a technique to be encouraged.

To be able to draw the right thermodynamic conclusions from the data obtained without supporting electrolyte, the potential axis for the waves should be appropriately corrected for ohmic drop. This problem has been addressed, and interesting solutions suggested by Bento et al. [95,96].

## 9. Polyelectrolytes and colloids

Voltammetry at microelectrodes without supporting electrolyte has been introduced as a very useful technique for studying the transport of electroactive ions and molecules in such complex systems as solutions of polyelectrolytes, large polymer molecules with one or more ionic groups per monomer unit [40,97–102], colloidal suspensions [103–105], and polymeric gels [106]. The electrostatic interactions between a polyelectrolyte and simple counterions are the strongest in solutions of very low ionic strength. These interactions affect the diffusion coefficients of the counterions strongly, and therefore, can be evaluated by measuring the changes in the diffusion coefficients. Since the steady-state current at a microelectrode is directly proportional to the diffusion coefficient of a counterion, voltammetric techniques bring to these studies good accuracy and high

precision. It has been demonstrated that voltammetric results obtained in polyelectrolyte solutions are free from experimental artifacts connected with the interfacial nature of the measurements, and the diffusion coefficients measured by voltammetry agree well with self-diffusion coefficients determined by an independent method, pulsed-field-gradient spin-echo NMR [99]. The cost and complexity of voltammetric experiments are negligible in comparison with radioactive tracer and pulsed-field-gradient spin-echo NMR methods, which have been used so far to determine transport of counterions in polyelectrolyte systems [107–109].

The voltammetric studies of the counterion transport in polyelectrolyte solutions have been based on comparison of the diffusion coefficient of a counterion in polyelectrolyte solution with that in simple solution. The procedure has involved the following steps: (i) determination of  $D$  of the counterion in polyelectrolyte solution over a wide range of concentrations of supporting electrolyte; (ii) determination of  $D_0$  of the same ion in simple, nonpolyelectrolyte solution for the same concentrations of supporting electrolyte; (iii) comparison of the  $D$ -values from polyelectrolyte solution with that from simple solution. Two techniques have been used to study the transport of counterion in polyelectrolyte solutions. First, the transport of the hydrogen counterion, the product of the dissociation of a polyacid, was determined from the steady-state reduction currents of  $\text{H}^+$  at platinum microelectrodes. In solutions without or with a low level of supporting electrolyte, the limiting steady-state current is controlled by both diffusional and migrational transport of the electroactive ion. The second technique introduces the concept of the probe counterion [98,99,101,102]. The use of metal cations such as  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  as electroactive probe counterions in PSSA solutions has been proposed. The concentration of the probe counterion should be much lower than the concentration of polyacid to give the same interactions between the polyion and both hydrogen (from the dissociation of PSSA) and metal counterion. Additionally, if the concentration of probe counterion is at least 50 times lower than the concentration of native counterion, the latter acts as the supporting electrolyte for the metal ion, and the transport-limited steady-state current of the reduction of the metal probe cation is not larger than 1.005 times the diffusional value [36].

It has been found that the diffusion coefficient of monovalent counterions,  $\text{H}^+$  and  $\text{Tl}^+$ , in poly(styrene-sulfonic acid), PSSA, solution without supporting electrolyte is 0.35 of that in simple acid solution. The transport of multicharged cations in this medium is suppressed even more. The diffusion coefficient of the divalent counterions,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , in PSSA solutions without electrolyte was 0.06 of the value in the simple solution. The dependence of the normalized

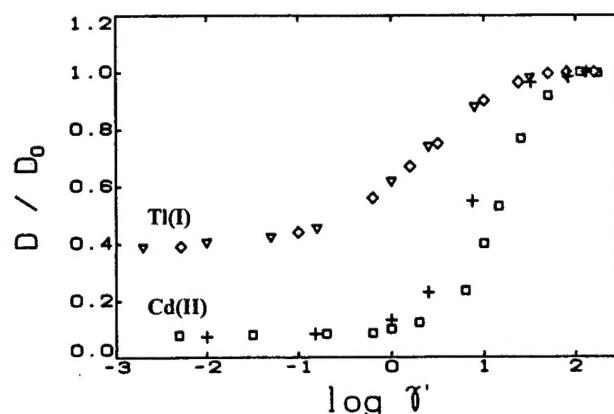


Fig. 6. Transport of  $\text{Tl}^+$  and  $\text{Cd}^{2+}$  probe ions in poly(styrenesulfonic acid), PSSA, solutions and its dependence on concentration of electrolyte,  $\text{LiClO}_4$ . 0.1 mM  $\text{Tl}^+$  in 20 mM PSSA ( $\diamond$ ), 0.05 mM  $\text{Tl}^+$  in 2 mM PSSA ( $\nabla$ ), 0.1 mM  $\text{Cd}^{2+}$  in 20 mM PSSA ( $\square$ ), and 0.05 mM  $\text{Cd}^{2+}$  in 2 mM PSSA (+).  $\gamma' = c_{\text{SE}}/c_{\text{PSSA}}$ ,  $D$ -diffusion coefficient in PSSA solution,  $D_0$ -diffusion coefficient without PSSA.

diffusion coefficient in polyelectrolyte solution, which is the ratio of the diffusion coefficient in PSSA to that in simple solution,  $D/D_0$ , on the concentration of supporting electrolyte given as the support ratio,  $\gamma = c_{\text{PSSA}}/c_{\text{SE}}$ , is presented in Fig. 6. As one can see the diffusion coefficient of the probe ion increases with addition of electrolyte, and for sufficient excess supporting electrolyte it reaches a value identical to the diffusion coefficient in a solution without polyelectrolyte.

## 10. Analytical applications

In chemical analysis and especially in trace analysis, an addition of supporting electrolyte may introduce unwanted impurities to the sample. However, some unknown ions are always present in the solution, even if no supporting electrolyte is added. One or more of those ions neutralize the excess charge produced at the surface of the electrode by the reduction/oxidation process of the uncharged reagent. This may lead to unexpected complications. Therefore, in some cases, it might be reasonable to add a very small amount of a chosen salt (to a level exceeding several times that of the unknown counterion). This addition will clarify the process of accumulation of counterions.

### 10.1. Anodic stripping

Anodic stripping studies are very important from the analytical point of view, especially in environmental analysis of natural waters. The deposition process is usually not complicated in solutions without supporting electrolyte. Some problems may appear in the interpretation of the stripping peaks. This is related to the fact, that during the oxidation of the preconcentrated metal

from the electrode the counterions are drawn from the solution, their identity is often not known, and the concentration of both cation and counterion at the electrode surface at the peak potential are very high. Therefore, the type of the counterion in a particular water sample should have an influence on the peak position and width.

A review on the present status, perspectives and challenges of in situ voltammetric measurements in natural waters is given by Tercier and Buffle [110]. An in situ analysis of water in lakes or seas is technically easier without the step of addition of supporting electrolyte. Buffle and co-workers [111,112] have proposed the use of an iridium-based mercury-plated microelectrode to determine trace metals at nM concentration levels. These electrodes have been shown to give analytically reproducible results and may be used in low-ionic-strength media such as lake waters. Nanomolar concentrations of  $\text{Pb}(\text{II})$  and  $\text{Cd}(\text{II})$  were determined in solutions of the lake water without added electrolyte.

Anodic stripping determination of cadmium and lead in pure water, of conductivity as low as  $0.6 \mu\text{S cm}^{-1}$ , was studied by Daniele and Mazzocchin [113] at a mercury microelectrode based on a platinum disk electrode. The anodic stripping peaks were investigated in detail to examine the influence of the solution resistance and migration on the peak position, peak width at half-height,  $w_{1/2}$ , and peak current. The results show that the presence of a small ohmic drop leads to larger  $w_{1/2}$  values than those obtained in the presence of supporting electrolyte, while the peak position varies slightly as a consequence of a change in the liquid junction potential. In a series of papers, Daniele et al. [114–118] presented voltammetry at microelectrodes in solutions without added supporting electrolyte as a successful technique for the determination of heavy metals and other components in such natural samples as rain, and sea water, wine and milk.

Nyholm and Wikmark [119,120] presented the results of the anodic stripping voltammetric studies of copper (II), lead (II) and mercury (II). The determination of copper ions with mercury-coated carbon fiber microelectrodes formed ex-situ was performed with a low concentration of supporting electrolyte. The experiments showed that the copper peaks were broad and non-symmetrical when the concentration of electrolyte was less than ca.  $10^{-6} \text{ M}$ , despite the fact that well defined peaks were still obtained for lead. An addition of a small amount of  $\text{NaNO}_3$  was found to increase the reproducibility of the measurements, particularly in the differential-pulse mode;  $5 \times 10^{-10} \text{ M} \text{ Cu}^{2+}$  could be determined with a deposition time of 1800 s in the presence of  $2.5 \times 10^{-6} \text{ M} \text{ NaNO}_3$ . As the authors suggested, two other factors in addition to migration influence the stripping peak shapes and potentials; double-layer structure and supersaturation of the mercury

film. A very low concentration of lead ion,  $3.2 \times 10^{-11}$  M, was also determined successfully by Wong and Ewing [121] using anodic stripping voltammetry without added supporting electrolyte at ultrasmall carbon ring electrodes coated in situ with mercury.

### 10.2. Other applications

Interesting applications of voltammetry with microelectrodes without supporting electrolyte were proposed by Perdicakis et al. [44,122]. The authors have determined acid numbers of fluid lubricants, phosphate esters, based on the reduction steady-state currents of hydrogen ion at platinum microelectrodes in solutions without supporting electrolyte. The authors also studied the partition reaction of  $\text{Bu}_4\text{NI}$  and  $\text{Et}_4\text{NPic}$  between phosphate buffer and dichloromethane without adding supporting electrolyte. Extraction and dissociation constants were determined by voltammetry in the organic phase.

Voltammetry with microelectrodes without or with very low levels of supporting electrolyte was also used for the determination of water in acetone solutions of such samples as acetone itself, butter, oil and inorganic salts [123], determination of anthracene and phenanthrene in chlorobenzene solutions [35], and determination of alkyl iodides in propylene carbonate [32].

Jiang et al. [124] have shown that well defined voltammograms with good reproducibility can be obtained without supporting electrolyte by use of a composite microdisk electrode (Nafion® 117/Cu). The measured current of nitrobenzene in methanol was dependent on dissolution and transport rate in the membrane; however it is proportional to the concentration of the analyte in the organic solvent over a wide range.

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